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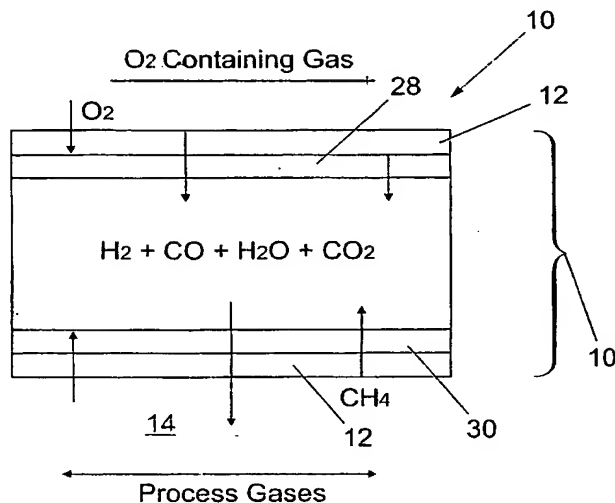
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(54) Title: A MEMBRANE APPARATUS AND METHOD OF PREPARING A MEMBRANE AND A METHOD OF PRODUCING HYDROGEN



(57) Abstract: The present invention discloses a method, apparatus and method of manufacturing an apparatus; all to produce hydrogen gas, particularly synthesis gas. Preferred embodiments of the invention include an alpha alumina membrane which has been treated with a TiO₂ wash coat on one side and has an active gamma alumina layer on an opposite side. A metal catalyst, preferably rhodium, is deposited within the pores of the alumina. Oxygen travels through the membrane and is activated before contacting methane on the other side of the membrane and forming synthesis gas through partial oxidation of the methane. Embodiments of the invention have a number of benefits including the high conversion rate of oxygen (100 %), the separate feed streams of methane and oxygen which allow for optimal ratios to be used without danger of explosion, and the opportunity to vary the feed rates without changing the products

formed. Normally gaseous hydrocarbons recovered from remote oil wells (e.g. offshore oil wells) can thus be converted to synthesis gas and then to normally liquid hydrocarbons via a Fischer-Tropsch type reaction. The normally liquid hydrocarbons are easier to transport away from the remote oil well than normally gaseous hydrocarbons.



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1 A Membrane Apparatus and Method of Preparing a
2 Membrane and a Method of Producing Hydrogen

3
4 The present invention relates to a membrane and a
5 method of preparing the membrane, the membrane being
6 particularly, but not exclusively, useful in
7 producing synthetic gas for use in Fischer-Tropsch
8 gas-to-liquids production in the oil and gas
9 exploration industry or for producing hydrogen for
10 use as a fuel.

11
12 While offshore oil production has risen slightly in
13 recent years, natural gas (which mainly consists of
14 methane) production has seen a marked increase.
15 Natural gas is often extracted during the extraction
16 of liquid hydrocarbons, such as oil, from the ground
17 and is often undesirable due to the lack of
18 infrastructure to transport the natural gas to an
19 onshore location. The lack of infrastructure can be
20 explained by the physical nature of natural gas
21 which makes it difficult to transport safely and/or
22 efficiently in its basic gaseous state. As a result

1 the natural gas is often flared (ignited) causing
2 economic waste and environmental concern. It would
3 therefore be desirable to either convert the natural
4 gas into some other substance which can be
5 transported easily, or transport the natural gas in
6 a liquid state. In this way, new field development
7 will be more financially viable through the use of
8 the extensive infrastructure and technology already
9 in place in the offshore industry for transporting
10 liquid hydrocarbons.

11
12 It is known to transport natural gas as a Liquid
13 Natural Gas (LNG) in specifically constructed
14 containers onboard vessels which have been adapted
15 for such purposes. However, this has many
16 disadvantages including; the need for expensive
17 pressurising equipment which is difficult to scale
18 down to suit smaller production fields, loss of gas
19 during transportation ("boil-off"), danger posed in
20 transit to vessel and crew by high pressure, highly
21 flammable gases and the requirement to depressurise
22 the LNG into a usable gaseous state at the customer
23 end.

24
25 It is considered that a better way of utilising
26 offshore produced natural gas (CH₄) is to convert
27 it, on or in close proximity to the offshore
28 production platform, into synthetic gas (syngas)
29 which can in turn be used to produce gases, fluids
30 and chemicals such as methanol, ammonia and
31 importantly, crude oil that can be readily pumped
32 through the same pipelines as the produced oil.

1 Syngas comprises a mixture of carbon monoxide(CO)
2 and hydrogen(H₂) .

3

4 By way of background information to the reader,
5 conversion of syngas to liquid hydrocarbon is a
6 chain growth reaction between carbon monoxide and
7 hydrogen on the surface of a heterogeneous catalyst.
8 The catalyst is either iron or cobalt based and the
9 reaction is highly exothermic. The temperature,
10 pressure, and catalyst determine whether a light or
11 heavy syncrude is produced. For example at 330°C
12 mostly gasoline and olefins are produced whereas at
13 180°C to 250°C mostly diesel and waxes are produced.
14 There are two main types of Fischer-Tropsch
15 reactors. The vertical fixed tube type has the
16 catalyst in tubes that are cooled externally by
17 pressurised boiling water. In large plants, several
18 reactors arranged in parallel may be used,
19 presenting energy savings. Another process uses a
20 slurry reactor in which pre-heated syngas is fed
21 into the bottom of the reactor and distributed into
22 the slurry which consists of liquid wax and catalyst
23 particles. As the syngas bubbles upwards through
24 the slurry, it is diffused and converted into more
25 wax by the Fischer-Tropsch reaction. The heat
26 generated is removed through the reactors cooling
27 coils where steam is generated for use in the
28 process. Again by way of background information to
29 the reader, this is shown in Fig. 7.

30

31 Thus if methane (or other gaseous hydrocarbons)
32 could be converted to syngas and thereafter to

1 liquid hydrocarbons, the transportation costs and
2 difficulties outlined above would be mitigated.

3

4 Synthesis gas can be made by partial oxidation of
5 methane (although it is more usually made by the
6 reaction of methane with steam under pressure.)

7

8 A major safety problem with the partial oxidation of
9 methane arises because methane and air (or oxygen)
10 should be fed into the reactor at the same time and
11 therefore there is the danger of an explosion.

12

13 It is known in the art that a reactor with
14 relatively dense ceramic membranes that conduct
15 oxygen can be used for syngas production (e.g. WO
16 98/48921 and WO 01/93987). These membranes generate
17 syngas by avoiding direct contact between the oxygen
18 and hydrocarbon feed, but this necessitates the use
19 of very high temperatures in order to achieve the
20 necessary oxygen flux. Moreover, being dense means
21 that the membrane has to be as thin as possible,
22 resulting in brittleness and crack formation, loss
23 of efficiency and reduced operating service life.
24 In some cases the membrane would need to be so thin
25 that it would be unable to support its own weight
26 and therefore impossible to use in practice.

27

28 Cost effective natural gas (methane) conversion to
29 syngas for gas-to-liquids production would therefore
30 be an important commercial development.

31

1 Hydrogen can be used as a clean fuel. However, the
2 amount of hydrogen that can be produced by using
3 renewable natural energy sources such as solar,
4 wind, and hydro-power is currently not sufficient to
5 satisfy demand. The utilisation of natural gas
6 and/or the production of hydrogen from natural gas
7 seen to be a viable alternative and the most
8 realistic solution at least in the first half of
9 this century [1, 2].

10

11 An example of progress in the widespread utilisation
12 of natural gas involves the development of small co-
13 generation system using the micro-gas turbine. In
14 addition, fuel cells are expected to be a highly-
15 efficient power generating system. The fuel cells
16 are anticipated to be deployed in residences in
17 addition to the installation in electrical vehicles.
18 Home-use of fuel cells can provide hot-water and
19 electricity, simultaneously. To commercialise the
20 stationary fuel cells, it is necessary to establish
21 alternative hydrogen generation technology.

22

23 According to a first aspect of the present invention
24 there is provided an apparatus comprising a first
25 chamber and a second chamber and a membrane which
26 divides the first and second chambers; the membrane
27 comprising an inorganic support and a catalyst;
28 the membrane being adapted to allow passage of a
29 first reactant from the first chamber to the second
30 chamber through said membrane;

1 wherein the first reactant is imparted with enough
2 energy by the catalyst upon said passage so as to
3 react with the second reactant.

4

5 According to a second aspect of the present
6 invention there is provided a method of preparing a
7 membrane, the method comprising:

8 providing a support; and
9 adding a catalyst to the support.

10

11 Preferably the first reactant is activated by being
12 imparted with enough energy by the catalyst upon
13 said passage so as to react with the second
14 reactant.

15

16 Preferably the energy imparted on the first reactant
17 activates molecules of the first reactant without
18 forming an ionic species, such as O^{2-} .

19

20 Preferably the support is adapted to operate at
21 temperatures exceeding 250°C.

22

23 Preferably the support comprises an inorganic
24 support.

25

26 Preferably, the membrane initially comprises an
27 inorganic coarse porous support. Most preferably,
28 the membrane initially comprises a ceramic coarse
29 porous support such as alpha alumina.

30

1 Preferably, the first coating alters the said
2 surface of the support and more preferably, the
3 first coating roughens the said surface.

4
5 Preferably, the first coating selectively alters the
6 size, and more preferably, the diameter and
7 tortuosity of the pores. Preferably, the first
8 coating is applied by dipping the support into a
9 solution which may comprise a wash coat solution
10 such as a retracting metal oxide solution. In a
11 preferred embodiment, the wash coat solution
12 comprises Titanium Dioxide (TiO_2). Typically, the
13 first coating is applied to an outer surface which
14 may be an outer cylindrical surface of the support.

15
16 Typically, the method further includes the step of
17 applying a second coating to a second surface of the
18 support, said second surface preferably being an
19 inner surface of the support and more preferably
20 being an inner surface of a bore of the support.
21 The second coating preferably comprises a flux
22 control layer and more preferably the second coating
23 is an inorganic porous layer. Most preferably, the
24 second coating comprises a gamma alumina layer.
25 Preferably, the second coating is applied by dipping
26 the support into a solution which may comprise a
27 boehmite solution.

28
29 Typically, the method further includes the steps of
30 drying the support and heating/firing the support.
31 Typically, the dipping-drying-firing sequence of the

1 second coating may be repeated a number of times as
2 required.

3
4 Preferably, the method further includes the step of
5 applying a catalyst to a surface of the membrane.
6 Typically, the catalyst is applied to the inner bore
7 of the pores of the membrane. Typically, the
8 catalyst comprises a metallic or non-metallic
9 catalyst, and is more preferably a metallic active
10 catalyst. Most preferably, the catalyst comprises
11 active rhodium. Alternatively the catalyst can
12 comprise nickel. Preferably, the catalyst is
13 applied to the said surface by passing an osmotic
14 solution over the said first surface, which may be a
15 first side, of the membrane and a cationic or
16 anionic catalyst precursor solution over the said
17 second surface, which may be the other side of the
18 membrane, such that the catalyst is deposited on the
19 inner bore of the membrane pores. Preferably, the
20 osmotic solution comprises different electrolytes
21 and non-electrolytes in an aqueous solution at room
22 temperature. More preferably, the osmotic solution
23 comprises a sucrose solution.

24
25 Preferably, the method further includes the step of
26 heating the membrane to a relatively high
27 temperature and may include the further step of
28 passing Hydrogen through the membrane pores such
29 that calcination occurs.

30

1 Preferably, the support may comprise one or more
2 inner structures such as struts to increase the
3 surface area of the inner surface of the inner bore.
4

5 According to a third aspect of the present invention
6 there is provided a method of producing hydrogen
7 gas, the method comprising:

8 providing a membrane, the membrane comprising a
9 support and a catalyst;

10 passing a first reactant through the membrane
11 from a first chamber to a second chamber; allowing
12 the first reactant to come into contact with the
13 catalyst upon passage through said membrane;

14 imparting the first reactant with enough energy
15 so as to react with the second reactant;
16 reacting the first reactant with a second reactant
17 to produce hydrogen gas.
18

19 Preferably, the membrane comprises a substantially
20 annular cylinder and more preferably, the first and
21 second chambers comprise a substantially cylindrical
22 cross section. More preferably, a sidewall of the
23 membrane separates the first and second chambers and
24 the second cylindrical chamber may be located within
25 the first cylindrical chamber.
26

27 Preferably, the second cylindrical chamber is
28 defined by an inner bore of the membrane.
29

30 Preferably, a portion of the membrane is permeable.
31 Alternatively, the entire membrane is permeable.
32

1 Preferably, the first reactant passes from the first
2 chamber through pores formed in the sidewall of the
3 membrane to the second chamber.

4

5 Alternatively, the second reactant passes from the
6 second chamber through the membrane to the first
7 chamber.

8

9 Preferably, the first reactant is oxygen and the
10 second reactant is a hydrocarbon. More preferably
11 the second reactant is methane. Typically, the
12 synthetic gas comprises carbon monoxide and
13 hydrogen.

14

15 An embodiment of the present invention will now be
16 described, by way of example only, with reference to
17 the accompanying drawings in which:

18

19 Fig. 1 is a transverse cross sectional
20 schematic view of a support of a membrane
21 apparatus in accordance with the present
22 invention;

23 Fig. 2A is a transverse cross sectional view
24 showing the support of Fig. 1 in more detail;
25 Fig. 2B is an end view of the support of Fig.
26 2A showing 'O' rings and cross sectional shape
27 of the support;

28 Fig. 3a is a diagrammatic cross sectional view
29 showing the formation of layers in the membrane
30 of the membrane apparatus of Figs. 2A and 2B;
31 Fig. 3b is a further diagrammatic cross
32 sectional view of the membrane apparatus;

1 Fig. 3c is a yet further diagrammatic cross
2 sectional view of the membrane apparatus
3 showing the movement of molecules in use;
4 Fig. 4 is a temperature / syngas ratio plot
5 showing the optimal temperature required to
6 achieve the desired syngas ratio;
7 Fig. 5 is a feed ratio / syngas ratio plot
8 showing the optimal feed ratio required to
9 achieve the desired syngas ratio; and
10 Fig. 6 is a % Vol. N₂ / Conversion plot showing
11 conversion of CH₄ and O₂ at 750°C;
12 Fig. 7 is a schematic flow diagram providing
13 background information relating to Fischer-
14 Tropsch Gas-to-Liquids Technology;
15 Fig. 8a is a graph showing the effect of
16 temperature on the methane conversion rate;
17 Fig. 8b is a graph showing the effect of
18 reaction temperature on the conversion rate of
19 methane for fixed-bed and membrane reactors;
20 Fig. 9 is a graph showing the yield of reaction
21 products at low methane conversation rates for
22 a membrane apparatus in accordance with the
23 present invention;
24 Fig. 10 is a graph showing the yield of various
25 reaction products at high methane conversion
26 rates by varying the feed ratio at a fixed
27 temperature;
28 Fig. 11 is a graph showing the yield of various
29 reaction products by varying the temperature at
30 a fixed feed ratio;

1 Fig. 12 is a graph showing the selectivity of
2 various reaction products at low methane
3 conversions;
4 Fig. 13 is a graph showing the selectivity of
5 various reaction products by varying the feed
6 ratio at a fixed temperature;
7 Fig. 14 is a graph showing the selectivity of
8 various reaction products by varying the
9 temperature at a fixed feed ratio;
10 Fig. 15 is a graph showing the yield of various
11 reaction products against the proportion of
12 nitrogen in a nitrogen/oxygen feed;
13 Fig. 16 is a graph showing the selectivity of
14 various reaction products against the
15 percentage of nitrogen in the nitrogen/oxygen
16 feed.
17 Fig. 17 is a graph showing the yield of various
18 reaction products against the percentage of
19 carbon dioxide in the methane feed; and,
20 Fig. 18 is a graph showing the selectivity of
21 various reaction products against the
22 percentage of carbon dioxide in the methane
23 feed.

24

25 A membrane apparatus 8 in accordance with the
26 present invention is shown in Fig. 1 and comprises a
27 tubular membrane 10 and an outer tubular shell 16.
28 Two gas flow passages are thus formed which are
29 substantially sealed off from each other. The first
30 within a bore 14 of the membrane 10 and the second
31 in the annulus 22 between the membrane 10 and the
32 shell 16.

1 The inner bore 14 of the modified membrane 10 may
2 have some supporting struts 34, as shown in Fig. 2.
3 These increase the structural strength of the
4 modified membrane 10. In operation, the struts 34
5 also change the flow pattern of oxygen flowing
6 through the sidewall 13 of the membrane 10 by
7 reducing the opportunity for the methane flowing
8 through the inner bore 14 to pass directly through
9 the centre of the modified membrane 10 inner bore
10 without coming into contact with the modified
11 membrane 10 surface. The struts 34 also increase
12 the internal surface area per unit volume of the
13 modified membrane 10, and hence increase the
14 opportunity for activation, compared to a completely
15 hollow cross section.

16
17 With reference to Fig. 3c, the modified membrane 10
18 comprises an α -alumina support 10, a TiO_2 washcoat
19 28 on the outer surface of the support 10 and a
20 γ -alumina layer 30 on the inside of the α -alumina
21 support 10. Rh catalyst particles 12 are
22 impregnated into the bores of the inner and outer
23 face of the sidewall 13 of the modified membrane 10.

24
25 Further layers of increasing pore radii may be
26 provided adjacent to the γ -alumina layer 30 and TiO_2
27 28 layers.

28
29 Referring to Figs. 2A, 2B and 3a-3b the preparation
30 of the membrane 10 layers will now be described.

31

1 The process starts with the inorganic (preferably
2 ceramic) coarse porous support 10. Supports of this
3 nature are now widely available and a wide variety
4 of companies currently supply these base materials
5 and a preferred support 10 comprises an alpha-
6 alumina tube having 10mm outer diameter and a 7mm
7 inner diameter, typically having a pore size of
8 between 110 and 180 nm. The support 10 comprises a
9 porous middle portion 11 which is typically around
10 300 mm in length, and two remaining non-porous
11 portions 26 of about 25 mm in length at each end of
12 the membrane 10. The end portions 26 are made non-
13 porous by glazing them with a sealant, such as SiO_2 -
14 BaO-CaO at 1100°C.

15
16 The wash coat 28 is then applied to the outer
17 cylindrical surface of the support 10 by dipping the
18 support 10 into a substance such as TiO_2 . This wash
19 coat 28 dipping step roughens the outer cylindrical
20 surface of the support 10 and adds microporosity to
21 the walls of the membrane catalysts 12. (In
22 operation the rough surface of the wash coat 28
23 forces the oxygen particles (not shown) to convolute
24 around the raggedness of the wash coat 12 and serves
25 to improve mass transfer of the limiting reactant
26 (oxygen) to the catalytic sites - this results in
27 improved syngas yields).

28
29 The oxygen flux control layer 30 is then applied to
30 the inside surface of the inner bore 14 of the
31 support 10. This layer 30 should be inorganic to
32 enable operation of the membrane 10 at high

1 temperatures and may comprise a gamma alumina layer
2 derived from a boehmite($\text{AlO}(\text{OH})$) solution with a
3 concentration of 0.6 mol/L. The inner surface of
4 the support 10 is exposed to the boehmite solution
5 via dipping for about 2 minutes. The support is
6 then air-dried overnight and then heated to between
7 700 - 750°C at a rate of 1°C / min. It may be
8 necessary to repeat this dipping-drying-firing
9 sequence for up to a total of three cycles to
10 achieve the required gamma-alumina layer thickness
11 on the support 10.

12
13 The deposition of the catalysts 12 on the support 10
14 is achieved using an osmotic ionic exchange process,
15 which will now be described.

16
17 Osmotic Ionic Exchanged Catalyst Deposition:

18
19 The catalysts 12 are prepared using either cationic
20 or anionic exchange using RhNO_3 or $\text{RhCl}_3 \cdot 2\text{H}_2\text{O}$
21 respectively in an organic medium (0.2g/L) as
22 precursors. Owing to the asymmetrical character of
23 the membrane as shown in Fig. 3a (i.e. wash coat 28
24 + support 10 + gamma alumina layer (boehmite) 30)
25 different ways of introducing the catalysts 12 to
26 the support 10 are utilised. In the first instance,
27 the osmosis process involves immersing the outer
28 surface of the partially modified membrane 10 in 6.0
29 molar sucrose solution, while the catalyst precursor
30 solution (e.g. RhNO_3 or $\text{RhCl}_3 \cdot 2\text{H}_2\text{O}$) is circulated
31 through the inner bore 14 of the partially modified
32 membrane 10. This configuration is reversed in the

1 second instance with the immersion of the outer
2 surface of the partially modified membrane 10 now in
3 a catalyst precursor solution and the osmotic
4 (sucrose) solution now circulated in the inner bore
5 14 of the partially modified membrane 10. The
6 membrane 10 is then washed using distilled water and
7 subsequently dried by blowing dry air either through
8 the inner bore of the now modified membrane 10 or
9 across the outer cylindrical surface.

10

11 Calcination (which involves heating the modified
12 membrane 10 to a very high temperature and then
13 passing Hydrogen through the modified membrane 10)
14 is then carried out under atmospheric pressure at
15 400°C for 2 hours. Metallic (active) Rh (the
16 catalyst 12) is obtained by reduction of Rhodium
17 ionic species using hydrogen at 400°C for 2 hours.

18

19 The modified membrane 10 characteristics may now be
20 measured. This may be done by scanning electron
21 microscopy (SEM) to show the degree of filling of
22 the modified membrane 10 pore network and to
23 estimate the gamma alumina (boehmite) layer 30
24 thickness.

25

26 Alternative materials may be selected. However it
27 is important that the selected materials have
28 similar thermal coefficients of expansion as
29 adjacent layers. If there is difference in thermal
30 expansion coefficients of the active porous layers
31 and porous support layers, there is an advantage in
32 selecting materials for the intermediate porous

1 support layers, with expansion coefficients which
2 gradually change from values near those for the
3 active porous layer to values near those for the
4 outer porous support layer. One way of achieving
5 this is to prepare the intermediate layers from a
6 mixture of the material used in forming active
7 porous layer decreasing in successive porous support
8 layers. For instance, porous support layer could
9 contain 75% by weight of the material used in
10 forming the active porous layer.

11
12 The above discussion does not exclude the use of
13 identical materials in active porous layer and
14 porous support layer. Such a material selection will
15 eliminate chemical incompatibility and differential
16 thermal expansion problems but typically entails
17 sacrifices in strength and material cost.

18
19 The number of porous support layers will depend on
20 the porous radius of the adjacent active porous
21 layer. They will vary from a single layer for
22 active porous layer pore radii selected from the
23 upper end of the specified range to four for pore
24 radii selected from the lower end of the specified
25 range.

26
27 The surface area of a material determines many of
28 its physical and chemical properties, including
29 water retention capacity and reactivity with
30 nutrients and contaminants. The BET Surface Area
31 Analyser can be used to estimate the specific
32 external surface of a solid by determining the

1 volume of a specific gas that is absorbed under
2 controlled conditions. The BET surface Area
3 Analyser has typically been used in routine
4 characterisation of various membrane materials and
5 synthetic mineral analogues important in process
6 engineering systems.

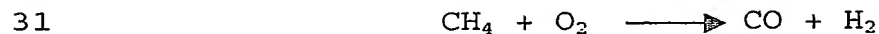
7
8 In the context of the present invention, BET surface
9 area analysis using nitrogen adsorption is used to
10 estimate the pore size distribution in the modified
11 membrane 10 and also to indicate values of porosity
12 and pore volume. Energy Dispersive X-Ray Analysis
13 (EDXA) surface analysis of the modified membrane 10
14 is used to confirm whether or not the modified
15 membrane 10 forms a continuous gamma alumina network
16 and the extent of any defects. It also provides
17 elemental composition of the catalysts 12 and its
18 relative dispersion. X-ray Photoelectron
19 Spectroscopy (XPS) is then used for chemical
20 analysis of the modified membrane 10.

21
22 It is recognised that the partial oxidation of
23 methane may occur via two distinct mechanisms, i.e.
24 direct partial oxidation or total oxidation followed
25 by reforming reactions.

26
27 To convert methane to syngas a partial oxidation is
28 required.

29

30



32

1 Should a full oxidation occur, the reaction products
2 would be CO₂ and H₂O.

3

4 The operation of the modified membrane 10 in the
5 membrane apparatus 8 will now be described.

6

7 An oxygen (O₂) supply 18 is fed into the outer bore
8 22 at one end of the membrane apparatus 8, and a
9 natural gas (which mainly comprises methane (CH₄))
10 supply 20 is fed into the corresponding end of the
11 inner bore 14.

12

13 The partial pressure of the oxygen 18 is maintained
14 at a higher pressure than that of the methane supply
15 20, which results in the oxygen passing through the
16 pores (not shown) of the modified membrane 10 from
17 the outer bore 22 to the inner bore 14. Upon doing
18 so, the oxygen molecules come into contact with the
19 catalysts 12 present in the sidewall 13 of the
20 modified membrane 10, which activates the oxygen
21 molecules before contacting the methane present in
22 the inner bore of the modified membrane 10. This
23 activation imparts sufficient energy on the O₂
24 molecule so that it can react at relatively low
25 temperatures without forming an oxygen ion.

26

27 When the activated oxygen molecules come into
28 contact with the methane molecules, syngas is
29 instantly formed according to the following chemical
30 reaction:-

31

32 $\text{CH}_4 + \text{O}_2^* \Rightarrow_{\text{catalyst}} \text{CO} + \text{H}_2.$

1 The produced syngas exits the membrane apparatus 8
2 from the other end of the inner bore 14 due to the
3 natural pressure differential created by the methane
4 supply 20, such that a syngas flow 24 is created.
5 Pneumatic control of the oxygen supply 18 flow rate
6 allows different flow rates of the methane supply 20
7 to be used, since an increase in the pressure of the
8 oxygen supply will result in a greater flux of
9 oxygen through the pores of the modified membrane
10 10.

11

12 In use a gas stream comprising the methane flows
13 next to or through the catalyst impregnated layer
14 12. The gamma alumina layer 30 on the bore side 14
15 enhances the reaction between permeated oxygen and
16 the methane. Since the oxygen molecules have to
17 diffuse to the bore side 14 of the gamma alumina
18 layer 30 and the adjacent porous layer, the gaseous
19 environment of the gamma alumina layer 30 at and
20 near the bore is less reducing than in the outer
21 porous layers. As a result a complete or partial
22 oxidation reaction will take place here with some
23 reforming occurring as gas moves away from the gamma
24 alumina layer 30 respectively. It is advantageous to
25 coat pores of the last porous support layer with the
26 reforming catalyst such as Rh to induce some
27 endothermic reforming as combustion products flow
28 through the porous support layer. This will assist
29 in removing the heat of the exothermic oxidation
30 reaction from the surface of the active porous
31 layer.

32

1 The gradient in oxygen activity in the porous layer
2 will prevent damage to the gamma alumina layer 30
3 from exposure to very low oxygen partial pressures,
4 thus permitting a greater degree of freedom in the
5 selection of materials for these layers.

6
7 Gas permeability through the modified membrane 10
8 can be measured by placing the end of the modified
9 membrane 10 sample tightly against the ends of the
10 outer tubular shell 16, with a seal being formed
11 therebetween by 'O' rings 32. A gas connection (not
12 shown) of the outer tubular shell 16 is attached to
13 a source of constant pressure. The predetermined
14 pressure difference being used creates a stable flow
15 of gas through the sidewall 13 of the membrane 10
16 sample, and is used to measure the flow rate, which
17 is proportional to the gas permeability of the
18 modified membrane 10.

19
20 Multi-component selectivity can be obtained by
21 measuring the individual species concentration in
22 the feed and permeate respectively.

23
24 Analysis of the reactants and products are analysed
25 using gas chromatography (GC) on-line using a 5 m
26 1/8 inch molecular sieve column to determine
27 methane, O₂, H₂ and CO. Any CO₂ will be analysed
28 using a separate 2 m long column of Porapak (RTM)
29 QS. In this analysis, a thermal conductivity
30 detector is also used. Water formed during the
31 reaction is condensed in an ice trap and further
32 removed by using a Drierite (RTM) trap.

1 In order to calibrate the chromatograph, multi-
2 component gas mixtures consisting of certified
3 compositions of methane, hydrogen, carbon dioxide,
4 carbon monoxide and oxygen were fed on one side of
5 the modified membrane 10 (e.g. the outer bore 22)
6 and the streams entering and exiting the inner bore
7 14 were analysed using the Thermal Conductivity
8 Detector (TCD) of a gas chromatograph.

9
10 Other aspects investigated in testing the membrane
11 10 include the effect of operating temperature (Fig.
12 4), methane flow rate (Fig. 5) and composition of
13 syngas yield and selectivity (Figs. 4 and 6).

14
15 Figs. 9-18 show a variety of these results using
16 such an apparatus. In each case, values of oxygen
17 and methane conversions and the yields of hydrogen
18 and carbon monoxide are monitored.

19
20 To investigate the initial reaction products of the
21 CH_4/O_2 feed, experiments were carried out at low
22 methane conversion rates and the products were
23 analysed as detailed above.

24
25 The oxygen feed flow rate was held constant at
26 75ml/min and the methane feed flow rate was varied
27 from 150 to 425ml/min, giving a range of total feed
28 flow rates from 225 to 500ml/min. The higher total
29 feed flow rate decreases the contact time of the
30 reactants with the catalysts, thereby decreasing
31 methane conversation.

32

1 In Fig. 8 it can be observed that for methane
2 conversion above and below 15% the CO₂ yield
3 increases significantly.

4
5 The CO yield by contrast, increases for conversions
6 lower than 20% having a slight decrease at
7 conversions around 16% increasing again thereafter.
8 The average CO yield is the highest average yield of
9 any one product. The water yield follows the same
10 profile as that for CO, but for methane conversions
11 around 18% it decreases again, deviating from the CO
12 yield. The average water yield is the lowest average
13 yield of any one product. The hydrogen yield is a
14 mirror image of the CO yield up to 16% methane
15 conversion, rising considerably for higher
16 conversion rates.

17

18 In a second experiment, the feed flow rate of oxygen
19 was varied from 15-75ml/min whilst the flow rate of
20 the methane was held constant at 150ml/min giving
21 reactions with total flow rates from 165-225ml/min,
22 as shown in Fig. 9. The temperature was 1023.15K.
23 The methane conversion decreases proportionally with
24 the increase in total flow rate, i.e. with the
25 decrease in contact time.

26

27 With higher methane conversions rates, allowing more
28 contact time, the CO₂ yield continues to increase up
29 to 30% methane conversion, falling slightly around
30 15% yield and significantly when methane conversions
31 reach around 50%. When methane conversion is over
32 55%, an insignificant yield of 5% CO₂ is found. Thus

1 the lowest yield of CO₂ is found for methane
2 conversion higher than 50%.

3

4 The CO yield stabilises at around 15% for methane
5 conversions higher than 20%. Water yield stabilises
6 at 5% for methane conversion from 20% up to around
7 40% increasing to almost 10% water yield at around
8 50% methane conversion, falling again to around 5%
9 yield at 55% methane conversion. Hydrogen yield
10 rises to around 18% hydrogen for methane conversions
11 from 30% up to 50% declining to 0.16 yield for
12 higher methane conversions.

13

14 Thus the contact time (controlled by the feed rate)
15 does not have a significant influence on the
16 resulting products, but does influence the methane
17 conversion rate. An advantage of certain
18 embodiments of the present invention is that they
19 can be used with low and high flow rates (producing
20 corresponding high and low contact times) without
21 affecting the resulting products. Longer contact
22 times aid methane conversion and provides high
23 yields of hydrogen and carbon monoxide and low
24 yields of water and carbon dioxide with methane
25 conversion is at about 50%.

26

27 To obtain this contact time the total feed flow rate
28 needs to be lower than 185ml/min for this load of
29 catalyst and temperature of 1023.15K. Other
30 embodiments of the invention can use different feed
31 flow rates.

32

1 It is well recognised that the partial oxidation of
2 methane may occur via two distinct mechanisms, i.e.,
3 direct partial oxidation or total oxidation followed
4 by reforming reactions [3]. In order to elucidate
5 the mechanism for the catalytic membrane reactor
6 used here, the effect of the temperature on the
7 methane conversion and product yields was studied.
8 The results of the analysis are presented in Figures
9 4 and 8a.

10

11 Fig. 8a shows the influence of temperature on
12 methane conversion and products yields for a total
13 feed flow rate of 165ml/min (150ml/min of methane
14 and 15ml/min of oxygen). Figure 8a shows that all
15 the oxygen is consumed. This occurs before
16 significant amounts of hydrogen and carbon monoxide
17 are formed. Another important feature is that the
18 conversion of methane, yield of water and yield of
19 hydrogen all pass through a maximum at 750°C. This
20 behaviour suggests that below 750°C, water, carbon
21 monoxide and hydrogen are primary products while
22 carbon dioxide is a parallel side reaction as
23 depicted in scheme 1.

24

25

26

27

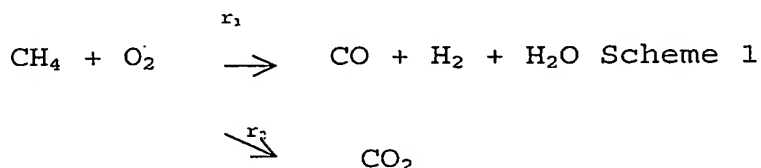
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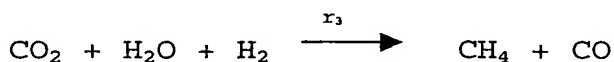
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32



Kinetic modelling has shown that the overall
reaction can be described well with the contribution
of parallel oxidation and full oxidation according
to scheme 1.

Above 750°C, the total oxidation reaction r_2 is expected to dominate with a significant increase in water and carbon dioxide. However, examination of Figure 8a shows that the carbon dioxide yield shows only a modest increase above 750°C, while the yields for water and hydrogen fall above this temperature. This suggests that hydrogen, carbon dioxide and water are being consumed accordingly to scheme 2 below.



Scheme 2

Scheme 2 helps explain the fall in the water and hydrogen yields, the modest CO_2 yield increase and the fall in methane conversion above 750°C.

One important aspect in the subsequent conversion of synthesis gas to liquids via a Fischer-Tropsch type reaction is the hydrogen: carbon monoxide ratio. A ratio of 2/1 is optimum for this conversion. From examination of Fig. 4 it can be seen that an optimal temperature of around 750°C results in the desired syngas (H_2/CO) ratio of 2.

The optimal feed ratio of methane to oxygen is shown, in Fig. 5, to be 10, although reasonable results which are relatively close to the desired ratio of 2 are obtained at feed ratios of between 2 and 6 also.

1 Figure 4 shows a plot of the H_2/CO over the
2 temperature range studied. The optimum for gas-to-
3 liquids conversion is obtained at a temperature of
4 $750^{\circ}C$. Above this temperature, a ratio below 2.0 is
5 attained while below $750^{\circ}C$, a value above 2.0 is
6 obtained.

7
8 Selectivity is defined as the yield of a particular
9 component in proportion to the amount of methane
10 conversion, that is

11

$$12 \quad \text{Selectivity}_x = \text{Yield}_x / \text{Conversion}_{CH_4}$$

13

14 Selectivity for low and high methane conversion
15 rates is shown in Figs. 12 and 13. There the CO
16 selectivity remains almost constant with values
17 around 0.9. This possibly indicates the absence of
18 secondary reactions for CO in low methane
19 conversions. Hydrogen selectivity decreases for
20 methane conversion up to 15% and increases
21 thereafter, reaching similar CO selectivity values.

22

23 Water selectivity profile follows a mirror image of
24 hydrogen selectivity, increasing for conversions up
25 to 15%, decreasing for higher conversions. For
26 higher values of methane conversion water
27 selectivity is constant, indicating the absence of
28 secondary reactions for water formation.

29

30 Hydrogen selectivity decreases significantly for
31 methane conversions up to 50%, increasing slightly
32 after that.

1 The selectivity of CO decreases to lower values than
2 H₂ selectivity for methane conversions up to 45%
3 becoming stable thereafter, indicating that for
4 methane conversions higher than 46%, CO is not
5 formed by any secondary reaction.

6
7 CO₂ selectivity decreases with the increase of
8 methane conversion, being the least selective gas
9 formed in this reaction.

10

11 It is important to note that the above-mentioned
12 experimental data were taken with varying contact
13 time, which can influence on the selectivity values.
14 For constant contact time, but varying temperature,
15 values are shown in Fig. 14.

16

17 Effect of Feed Composition Variation on Reactor 18 Performance

19

20 Figs. 15 and 16 show the yield and selectivity when
21 a varying proportion of nitrogen is added to the
22 oxygen feed. This influences the contact time of the
23 reagents with the catalyst.

24

25 Fig. 15 shows that CO yield falls constantly with
26 the addition of nitrogen in the system. Hydrogen
27 yield decreases with up to 50% nitrogen in the
28 oxygen feed and is constant thereafter.

29

30 The selectivity of carbon dioxide and water as shown
31 in the yield chart is not affected by the addition
32 of nitrogen in the system. However carbon monoxide

1 and hydrogen selectivities have a continuous drop
2 after a pick up at around 50% vol. of nitrogen.

3
4 The water and CO₂ yields values do not differ
5 significantly when nitrogen is present or absent
6 although there is a small rise for air composition
7 (80% N₂).

8
9 Fig. 6 also shows that even for an 80% vol N₂ feed
10 (and hence 20% O₂ feed) total oxygen conversion
11 takes place at a temperature of 750°C. The results
12 show that embodiments of the present invention can
13 work by using an air feed rather than a pure oxygen
14 feed thereby negating the need for an oxygen
15 separation plant for this reaction to take place.
16 This clearly reduces both the initial outlays and
17 operating costs of performing the reaction. Thus a
18 benefit of certain embodiments of the invention is
19 that air separation is not required to produce the
20 syngas of optimal ratio for onward reaction to
21 liquid hydrocarbons via a Fischer-Tropsch reaction.

22
23 In contrast to the nitrogen, the addition of CO₂ in
24 the feed does not influence CO yield, but reduces
25 hydrogen yield whilst increasing H₂O yield. The
26 results are shown in Figs. 17 and 18.

27
28 The selectivity of CO and H₂ decreases slightly in
29 higher proportion for hydrogen with the addition of
30 CO₂ in the methane feed.

31

1 The water selectivity is generally constant but does
2 increase slightly for higher amounts of CO₂ in the
3 feed.

4
5 An advantage of certain embodiments of the invention
6 is that the oxygen and methane are fed separately
7 into the apparatus and so there is no danger of an
8 explosion. The oxygen proceeds through the modified
9 membrane 10, is activated and then reacts when it
10 comes into contact with the methane. Thus it is
11 possible to lower the ratio of methane and oxygen in
12 the feed to a ratio more suitable for their
13 reaction. Such a ratio would normally be considered
14 potentially explosive, but certain embodiments of
15 the present invention allow for such ratios without
16 the potential for an explosion partly because of the
17 separate oxygen/methane feed.

18
19 Embodiments of the present invention benefit from
20 the highly dispersed catalyst which increase its
21 surface area and efficacy of the apparatus.

22
23 Embodiments of the present invention benefit from
24 the high conversion rate of oxygen. To illustrate
25 the benefits of membrane reactor operation in syngas
26 production, Figure 8b shows the effect of reaction
27 temperature on the conversion of methane over Ir-
28 loaded catalyst carried out with fixed-bed flow type
29 quartz reactor (350-10mm) at atmospheric pressure,
30 using 60mg of catalyst, 25 ml/min of O₂ and
31 temperature range of 673-873K. At 873K the
32 performance of Ir and Rh are roughly identical [4].

1 In the same figure, experimental data is shown for a
2 membrane system in accordance with the present
3 invention at 900.15K. The conversion values obtained
4 using a fixed-bed flow reactor are significantly
5 lower than those obtained in the membrane reactor
6 due to equilibrium limitation. This has been
7 overcome in the membrane reactor which achieves 100%
8 conversion of oxygen and a methane conversion of
9 41%.

10

11 Since, in the modified membrane 10, the catalysts 12
12 are highly dispersed, lower reaction temperatures
13 are feasible thereby reducing the propensity for
14 coke formation and subsequent deactivation of the
15 catalysts 12. The absence of coke formation
16 optimises catalyst usage whilst maintaining high
17 syngas selectivity. In the operation of the
18 membrane apparatus 8, additional catalysts (not
19 shown) may be inserted into the inner bore of the
20 modified membrane 10 as necessary to further enhance
21 the reaction. These additional catalysts (not
22 shown) are obtained by physically breaking another
23 sample of a modified membrane 10 into appropriate
24 particle sizes and inserting the particle sizes into
25 the test or operation sample.

26

27 Certain embodiments of the present invention benefit
28 from being used to generate hydrogen from, for
29 example, methane. The hydrogen can be used as a
30 fuel itself rather than converted into larger
31 hydrocarbons via a Fischer-Tropsch reaction.

32

1 Certain embodiments of the invention benefit from
2 the fact that the partial oxidation method is
3 exothermic and therefore reduces energy consumption.

4
5 Certain embodiments of the invention benefit from
6 the fact that the process has a fast start-up.

7
8 In contrast, steam reforming to produce syngas has a
9 large endothermic reaction and a slow start-up time.

10
11 Thus certain embodiments of the invention provide a
12 catalytic membrane reactor which has been developed
13 and used to produce hydrogen, particularly synthesis
14 gas; under various operating conditions with total
15 consumption of oxygen. At lower feed ratios (CH_4/O_2),
16 the syngas ratio is well above 2.0 while at higher
17 CH_4/O_2 ratio, the syngas ratio is 2.0. Thus depending
18 on the application the reactor is flexible to the
19 extent that it could be applied in the Fischer-
20 Tropsch process for converting natural gas to liquid
21 hydrocarbons. For gas-to-liquids conversion, an
22 optimum temperature of 750°C has been established at
23 which the hydrogen/carbon monoxide ratio is 2.0.

24
25 Modifications and improvements may be made to the
26 foregoing without departing from the scope of the
27 present invention. For example;

28
29 Though the apparatus and method described relates to
30 the production of syngas from the reaction between
31 methane and oxygen, a similar method and apparatus
32 could be used in the reaction of any light

1 hydrocarbon such as members of the alkane or alkene
2 group. Furthermore, the process and apparatus could
3 be used in any reaction where there are two
4 reactants which have constraints that make it
5 undesirable to mix them before the reaction has
6 taken place, such as flammability constraints.

7
8 It will be understood that the flux of oxygen could
9 be reversed by feeding the oxygen into the bore of
10 the modified membrane 10, and the methane into the
11 outer bore 22. However, in this case this
12 arrangement would be less desirable since the
13 methane may have impurities in it, such as H_2S ,
14 which would poison the catalyst 12. Therefore
15 passing the oxygen through the modified membrane 10
16 is preferred.

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- 12

1 Claims

2

3 1. An apparatus comprising a first chamber and a
4 second chamber and a membrane which divides
5 the first and second chambers; the membrane
6 comprising a support and a catalyst;
7 the membrane being adapted to allow passage of
8 a first reactant from the first chamber to the
9 second chamber through said membrane;
10 wherein the first reactant is imparted with
11 enough energy by the catalyst upon said
12 passage so as to react with the second
13 reactant.

14

15 2. Apparatus as claimed in claim 1, wherein the
16 support is adapted to operate at temperatures
17 exceeding 250°C.

18

19 3. Apparatus as claimed in claim 2, wherein the
20 support comprises an inorganic support.

21

22 4. Apparatus as claimed in any preceding claim,
23 wherein the support comprises pores and there
24 is a gradation in the average pore radii
25 towards one surface of the support.

26

27 5. Apparatus as claimed in any preceding claim,
28 wherein the membrane is adapted to activate
29 molecules of the first reactant without
30 forming an ionic species before the reaction
31 with the second reactant.

32

- 1 6. Apparatus as claimed in any preceding claim,
2 wherein the support comprises a layer with a
3 roughened surface which has an increased
4 tortuosity compared to the tortuosity of the
5 rest of the support.
6
- 7 7. Apparatus as claimed in claim 6, wherein the
8 relatively roughened surface is provided on an
9 outer surface of the support.
10
- 11
- 12 8. Apparatus as claimed in any preceding claim,
13 wherein a flux control layer is provided on
14 the support.
15
- 16 9. An apparatus as claimed in any one of claims 6
17 or 7, wherein a flux control layer is provided
18 on a first surface of the support and the
19 layer with a roughened surface is provided on
20 an opposite surface of the support.
21
- 22 10. Apparatus as claimed in claim 8 or 9, wherein
23 the flux control layer comprises an inorganic
24 porous layer which is adapted to hold a
25 portion of the catalyst therein and to control
26 the passage of the first reactant through the
27 membrane.
28
- 29 11. Apparatus as claimed in any one of claims 8 to
30 10, wherein the flux control layer is selected
31 from the group consisting of silica and gamma
32 alumina.

1 12. Apparatus as claimed in any preceding claim,
2 wherein the catalyst comprises a metal
3 catalyst.
4

5 13. Apparatus as claimed in claim 12, wherein the
6 metal catalyst is selected from the group
7 consisting of rhodium, ruthenium and nickel.
8

9 14. Apparatus as claimed in any preceding claim,
10 wherein the membrane is provided in the shape
11 of a cylinder.
12

13 15. Apparatus as claimed in any preceding claim,
14 wherein the membrane comprises one or more
15 struts.
16

17 16. Apparatus as claimed in any preceding claim,
18 wherein the support comprises alpha alumina.
19

20 17. A method of producing hydrogen gas, the method
21 comprising:
22 providing a membrane, the membrane comprising
23 a support and a catalyst;
24 passing a first reactant through the membrane
25 from a first chamber to a second chamber;
26 allowing the first reactant to come into
27 contact with the catalyst upon passage through
28 said membrane;
29 imparting the first reactant with enough
30 energy so as to react with the second
31 reactant;

1 reacting the first reactant with a second
2 reactant to produce hydrogen gas.

3
4 18. A method as claimed in claim 17, wherein the
5 energy imparted on the first reactant
6 activates molecules of the first reactant
7 without forming an ionic species before the
8 reaction with the second reactant.

9
10 19. A method as claimed in claim 17 or 18, wherein
11 the temperature is over 500°C.

12
13 20. A method as claimed in claim 19, wherein the
14 temperature is between 700°C and 800°C.

15
16 21. A method as claimed in any one of claims 17 to
17 20, wherein the first reactant is one of
18 oxygen and a hydrocarbon, and the second
19 reactant is the other of oxygen and a
20 hydrocarbon.

21
22 22. A method as claimed in claim 21, wherein the
23 oxygen and hydrocarbon do not come into
24 contact with each other until the first
25 reactant has passed through said membrane from
26 the first chamber to the second chamber.

27
28 23. A method as claimed in claim 21 or 22, wherein
29 the hydrocarbon comprises a normally gaseous
30 hydrocarbon.

31

1 24. A method as claimed in any one of claims 20 to
2 23, wherein the pressure within the first
3 chamber is greater than the pressure within
4 the second chamber.

5

6 25. A method as claimed in any one of claims 20 to
7 24, wherein carbon monoxide is formed in
8 addition to the hydrogen.

9

10 26. A method as claimed in claim 25, wherein the
11 carbon monoxide and hydrogen are further
12 reacted to produce normally liquid
13 hydrocarbons in a Fischer-Tropsch type
14 reaction.

15

16 27. A method as claimed in any one of claims 20 to
17 25, wherein the hydrogen is recovered for use
18 as a fuel.

19

20 28. A method of preparing a membrane, the method
21 comprising:
22 providing a support; and
23 adding a catalyst to the support.

24

25 29. A method as claimed in claim 28, wherein the
26 support is an inorganic support.

27

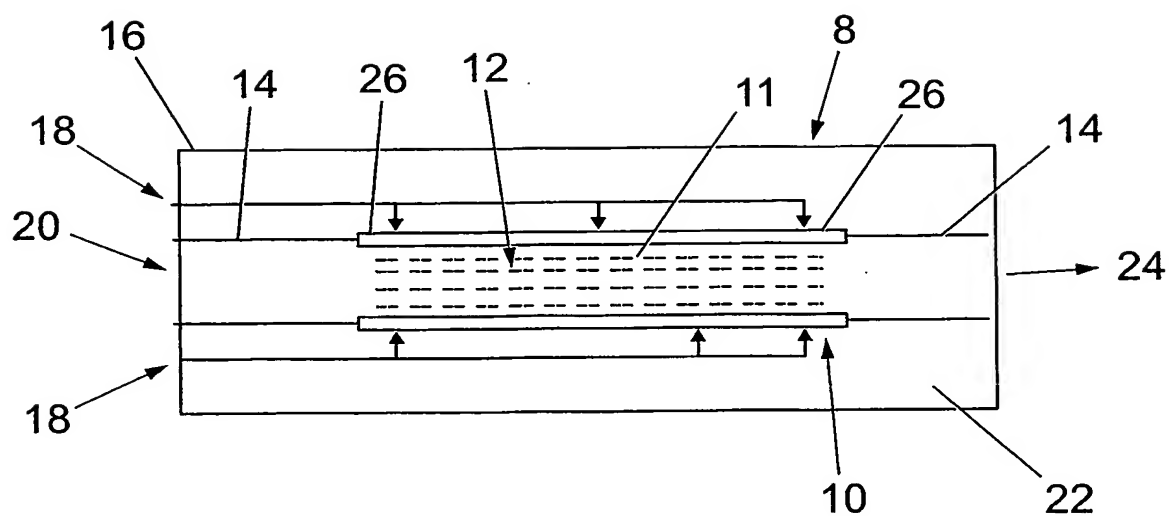
28 30. A method as claimed in claim 28 or 29, further
29 including the step of applying a coating to
30 one of the surfaces of the support.

31

- 1 31. A method as claimed in claim 30, wherein the
2 coating produces a roughened surface on the
3 support, said surface having an increased
4 tortuosity compared to the tortuosity of the
5 rest of the support.
6
- 7 32. A method as claimed in claim 30 or claim 31,
8 wherein the coating comprises a metal oxide or
9 metal oxide precursor.
10
- 11 33. A method as claimed in claim 32, wherein the
12 metal oxide or precursor comprises a group IV
13 metal oxide or group IV metal oxide precursor.
14
- 15 34. A method as claimed in claim 33, wherein the
16 group IV metal oxide or precursor comprises
17 TiO_2 or a TiO_2 precursor.
18
- 19 35. A method as claimed in claim 30, wherein the
20 coating produces a flux control layer on the
21 membrane.
22
- 23 36. A method as claimed in any one of claims 30 to
24 34, wherein a second coating, the second
25 coating being a flux control layer, is also
26 applied to the support.
27
- 28 37. A method as claimed in claim 35 or 36, wherein
29 the flux control layer is applied to the
30 membrane by exposure to a boemite sol.
31

- 1 38. A method as claimed in any one of claims 28 to
2 36 wherein the coating and/or the second
3 coating is applied by dipping the support into
4 a liquid comprising the coating.
5
- 6 39. A method as claimed in any one claims 28 to
7 38, including the step of applying the
8 catalyst to a surface of the membrane by
9 passing a catalyst precursor solution over a
10 first surface of the support and an osmotic
11 solution over the opposite surface of the
12 support, and allowing the catalyst or a
13 catalyst precursor to be deposited on the
14 support via the process of osmosis.
15
- 16 40. A method as claimed in any one of claims 28 to
17 39, further including the steps of drying the
18 support and heating/firing the support.
19

1 / 15

*Fig. 1*

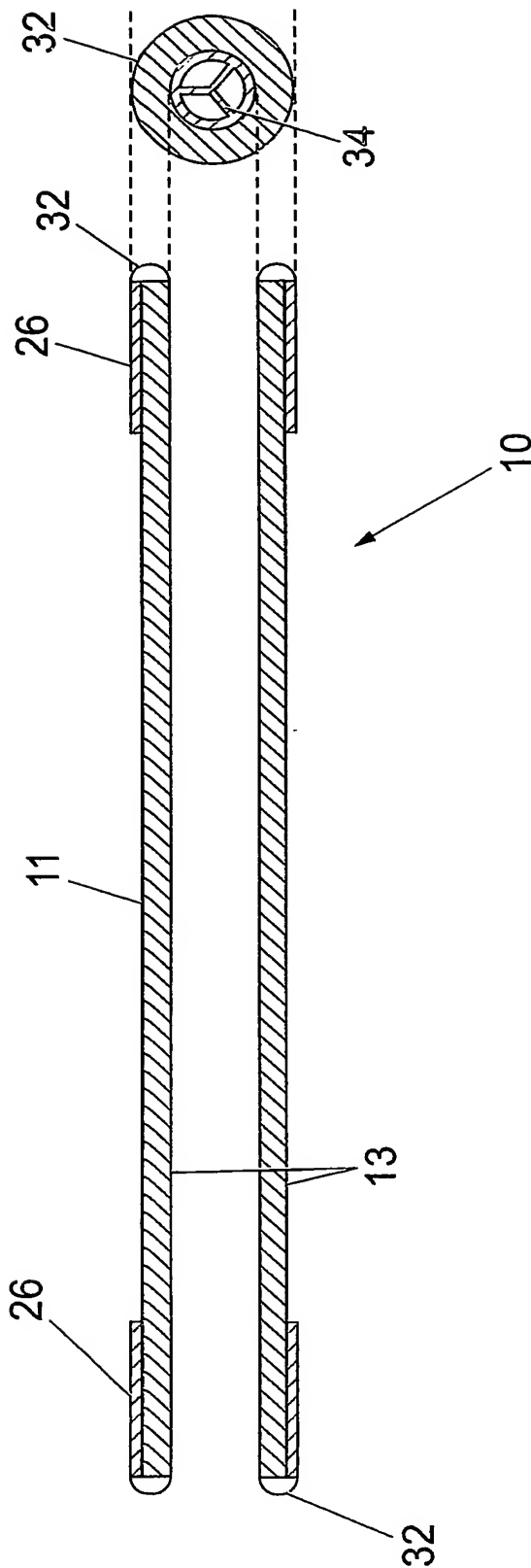
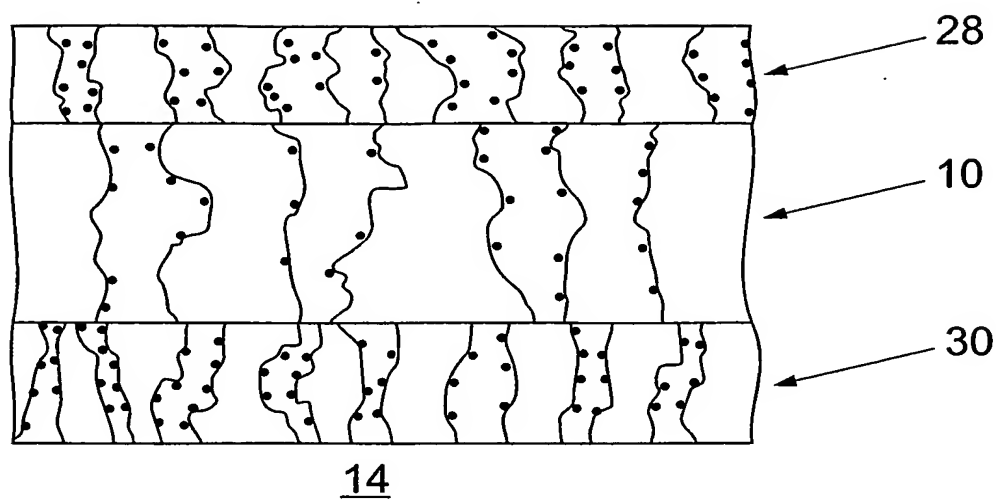


Fig. 2b

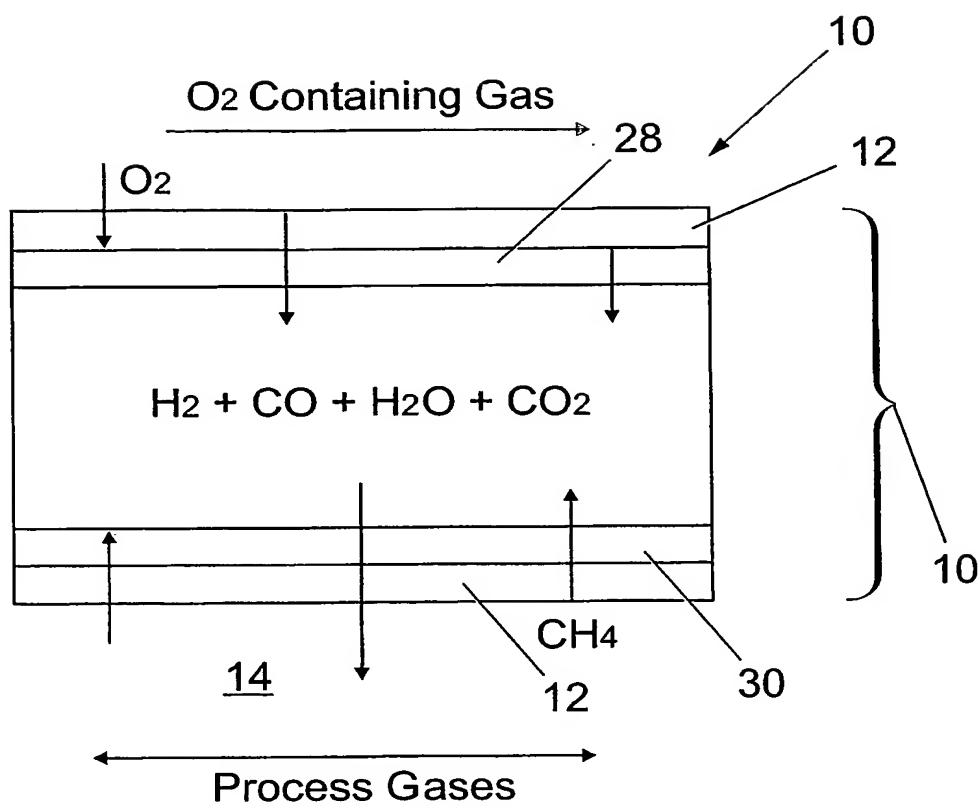
Fig. 2a

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*Fig. 3a*

4 / 15

*Fig. 3b*

20

5 / 15

(CH₄/O₂ feed = 150/15)

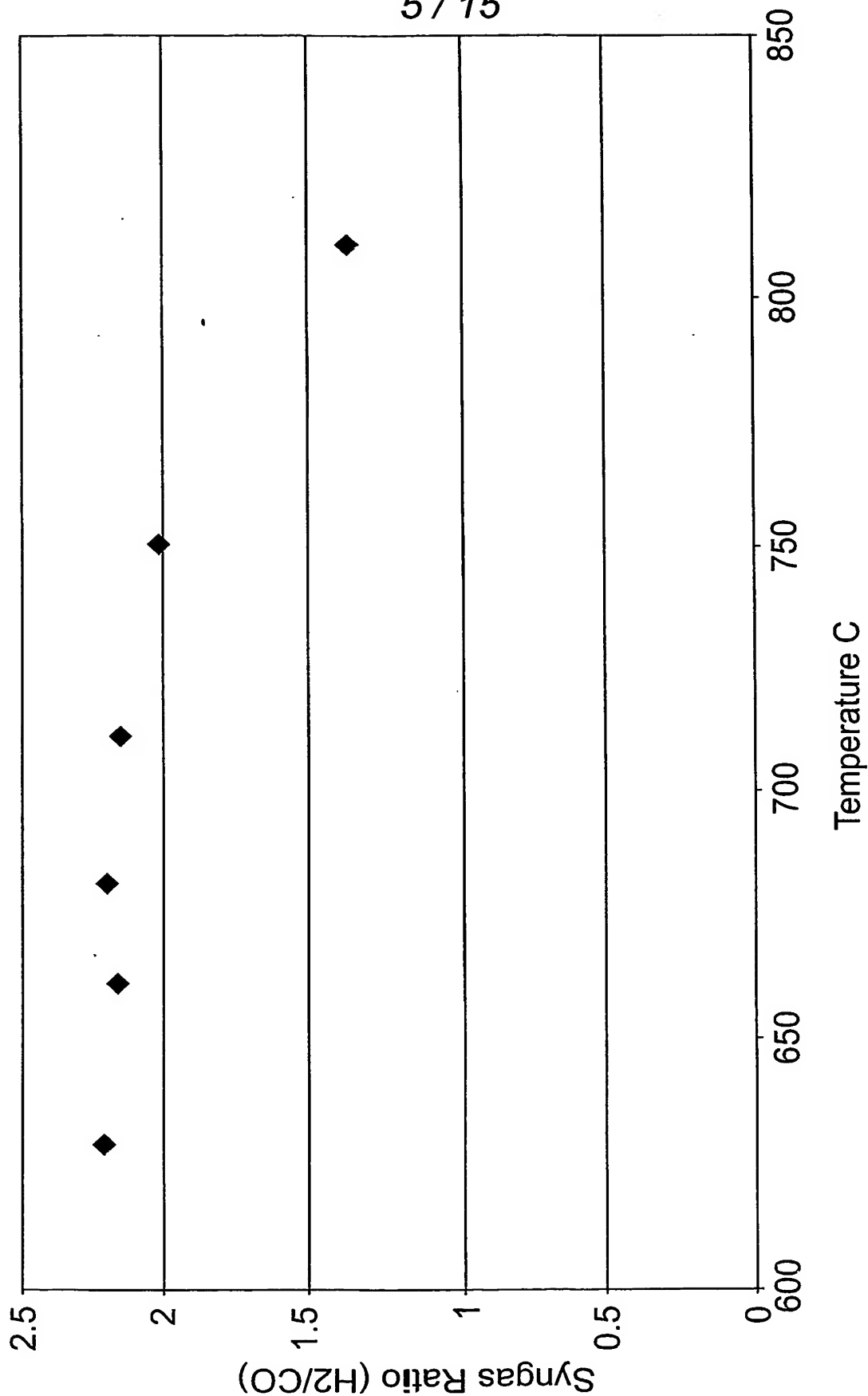
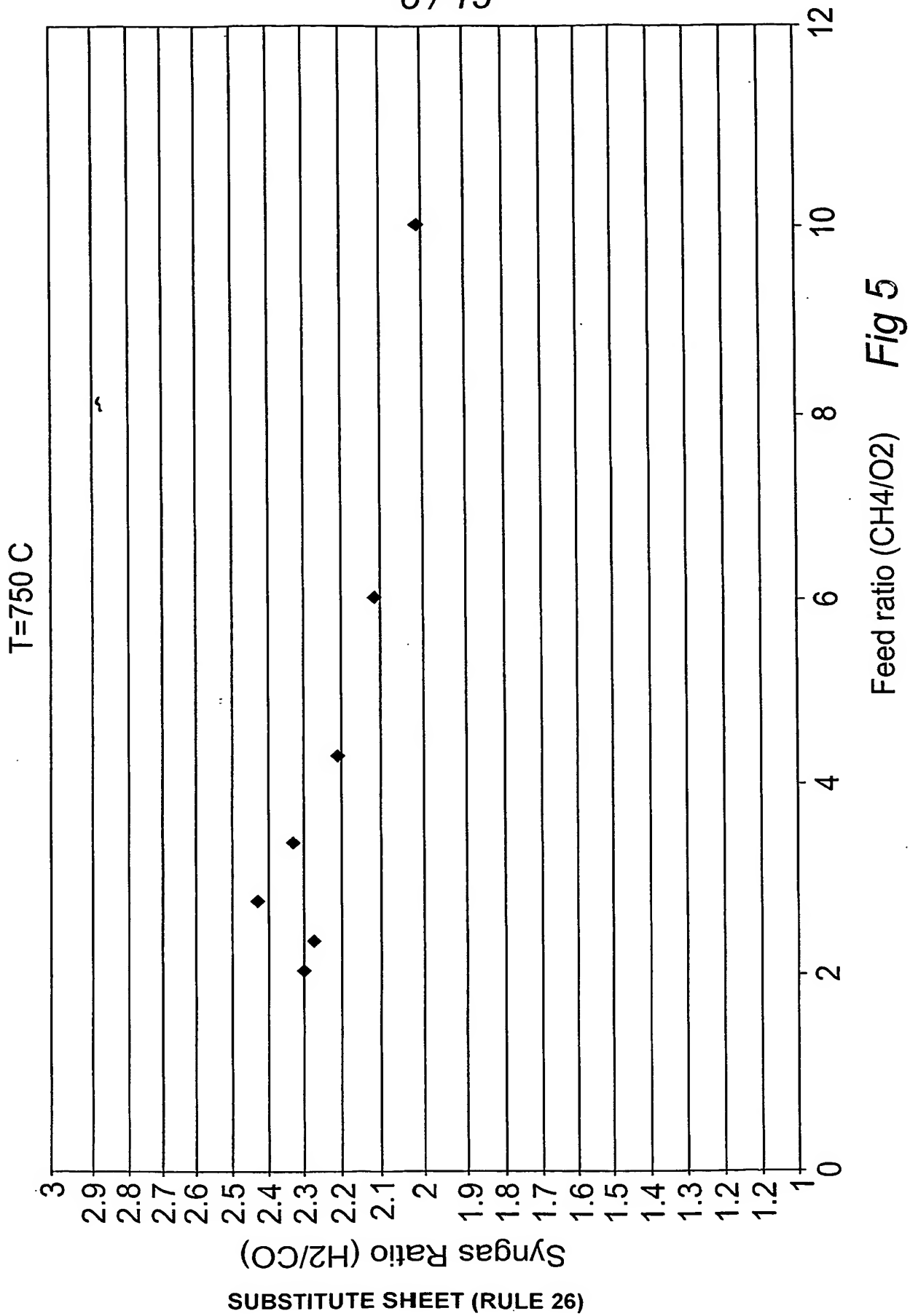


Fig. 4

33

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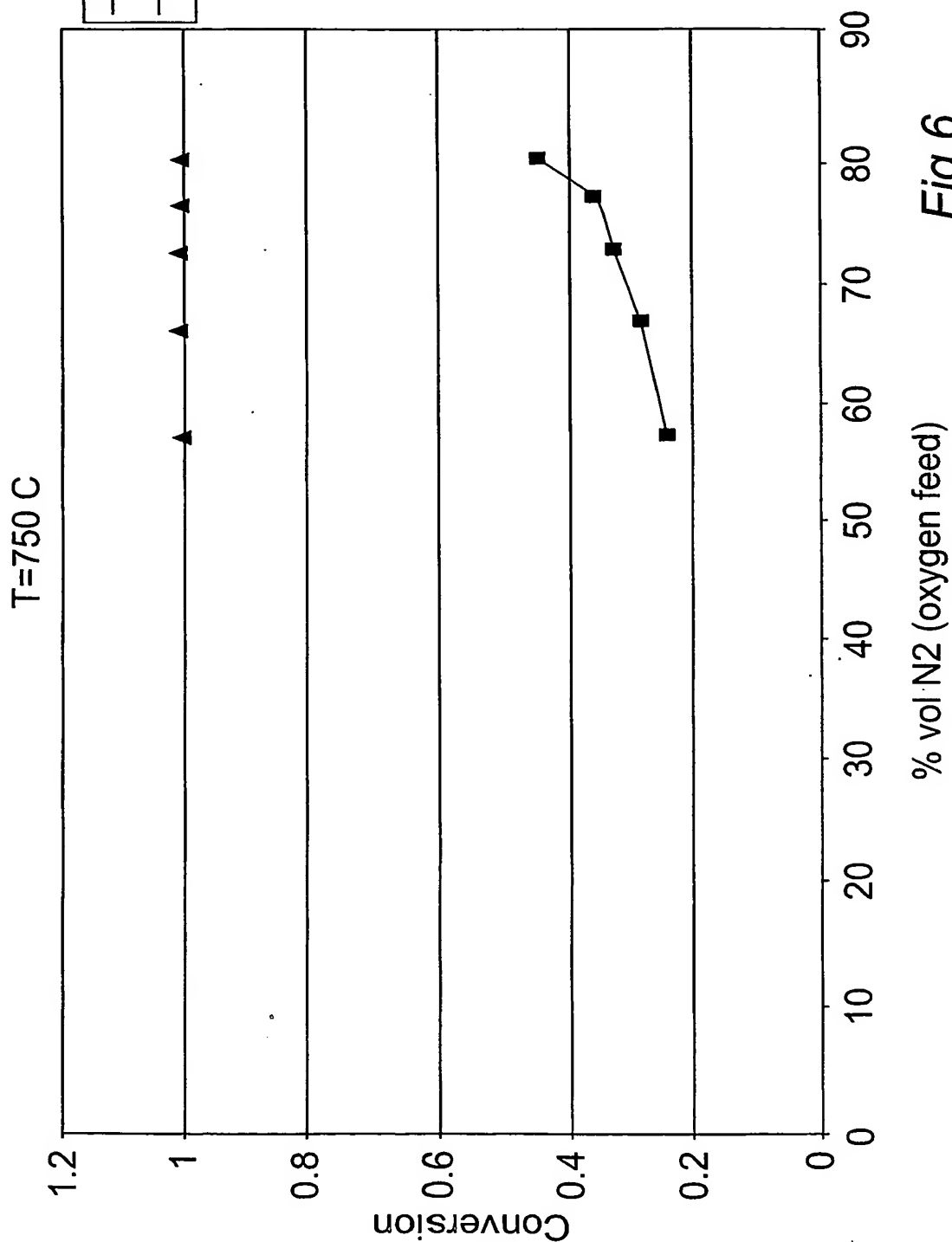


Fig 6

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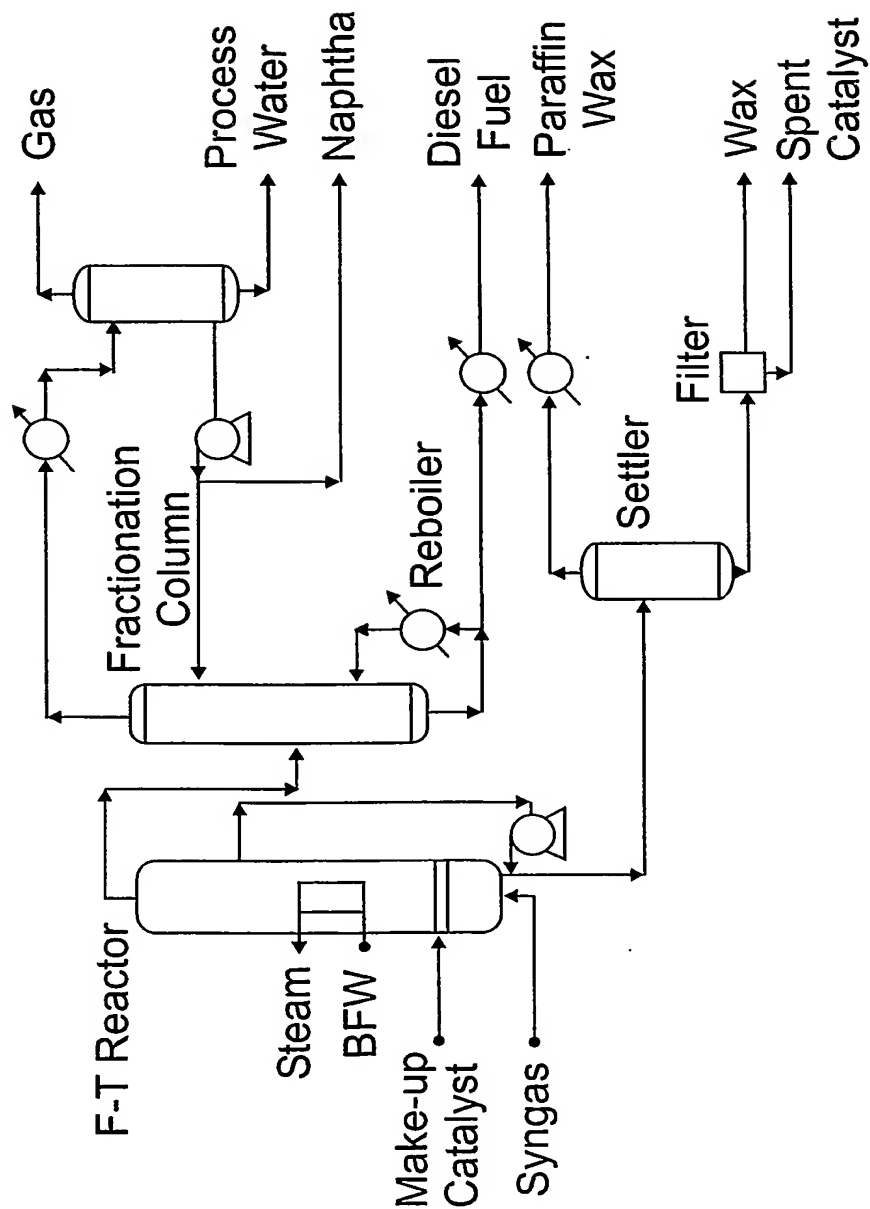


Fig 7

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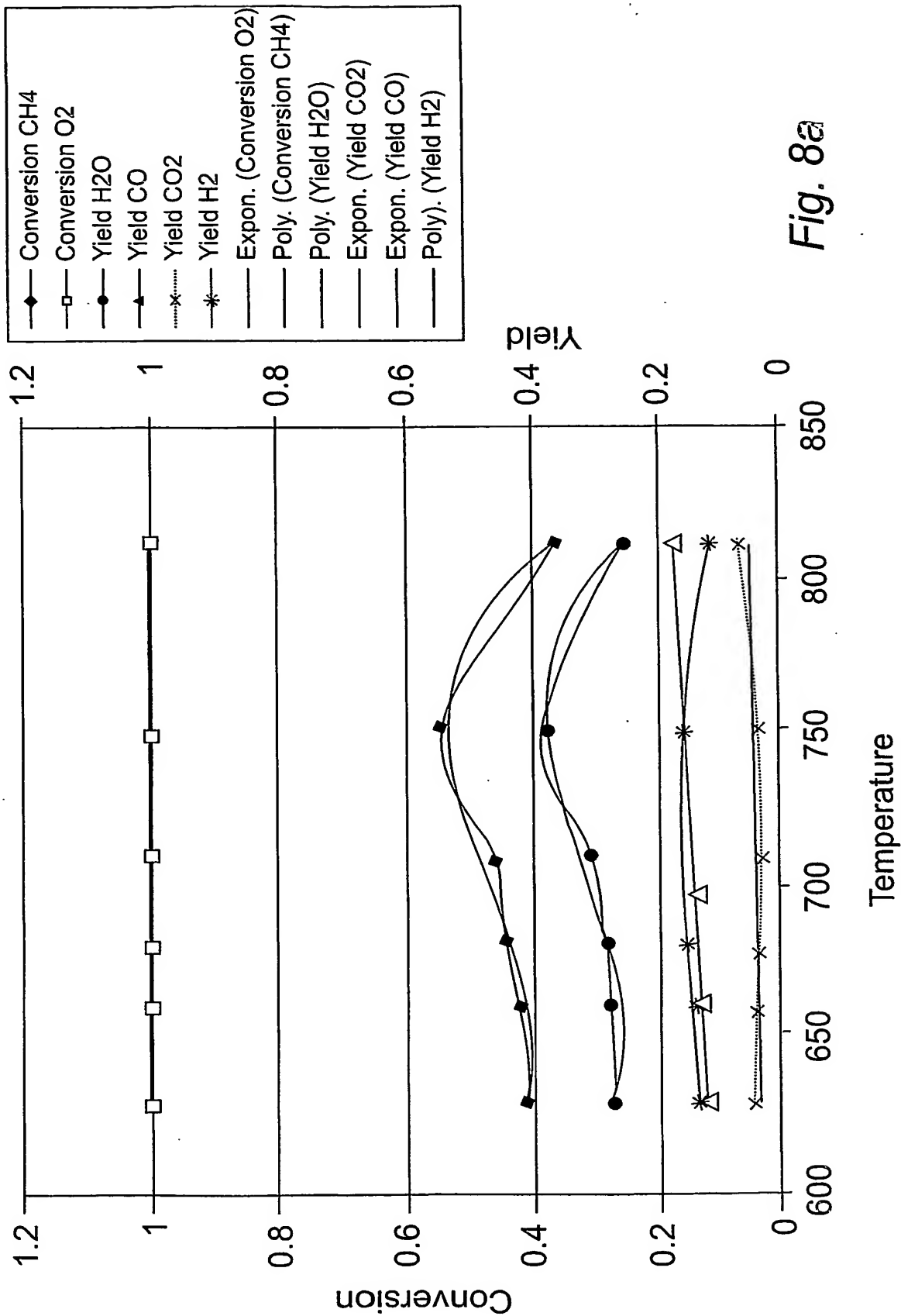
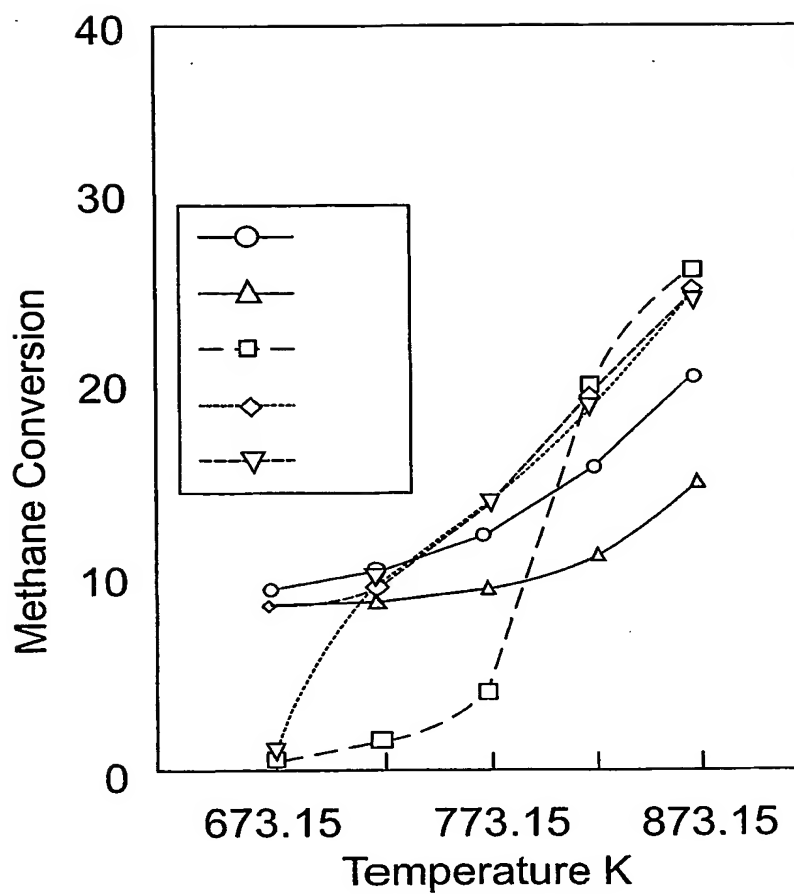


Fig. 8a

20

10 / 15

*Fig 8b*

11 / 15

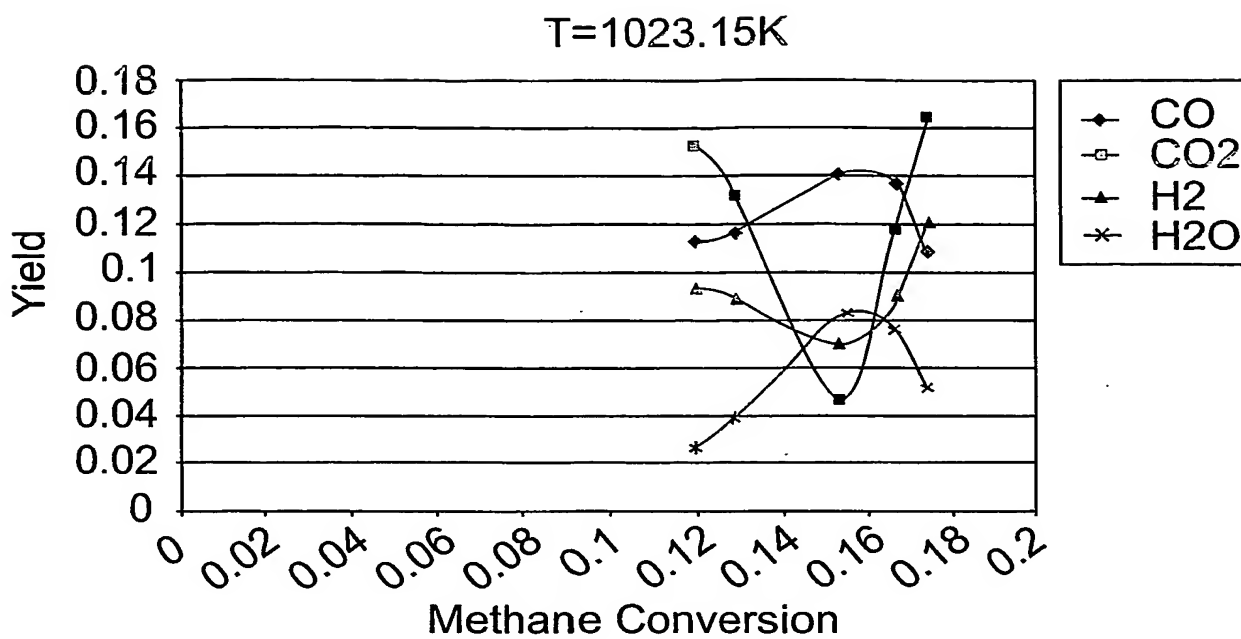


Fig. 9

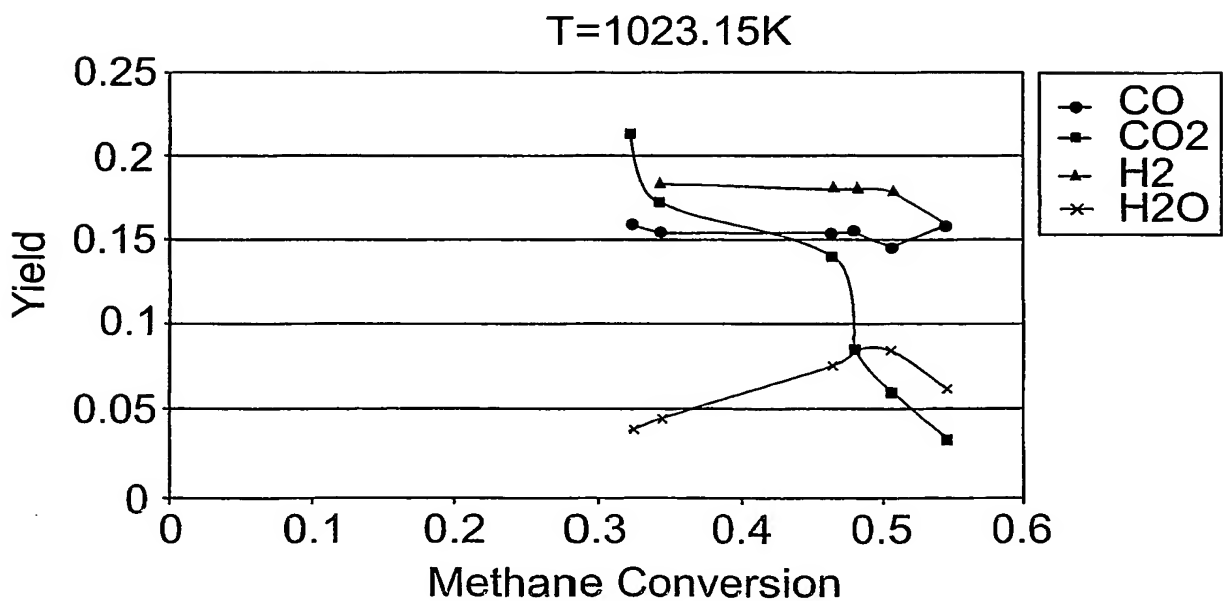


Fig. 10

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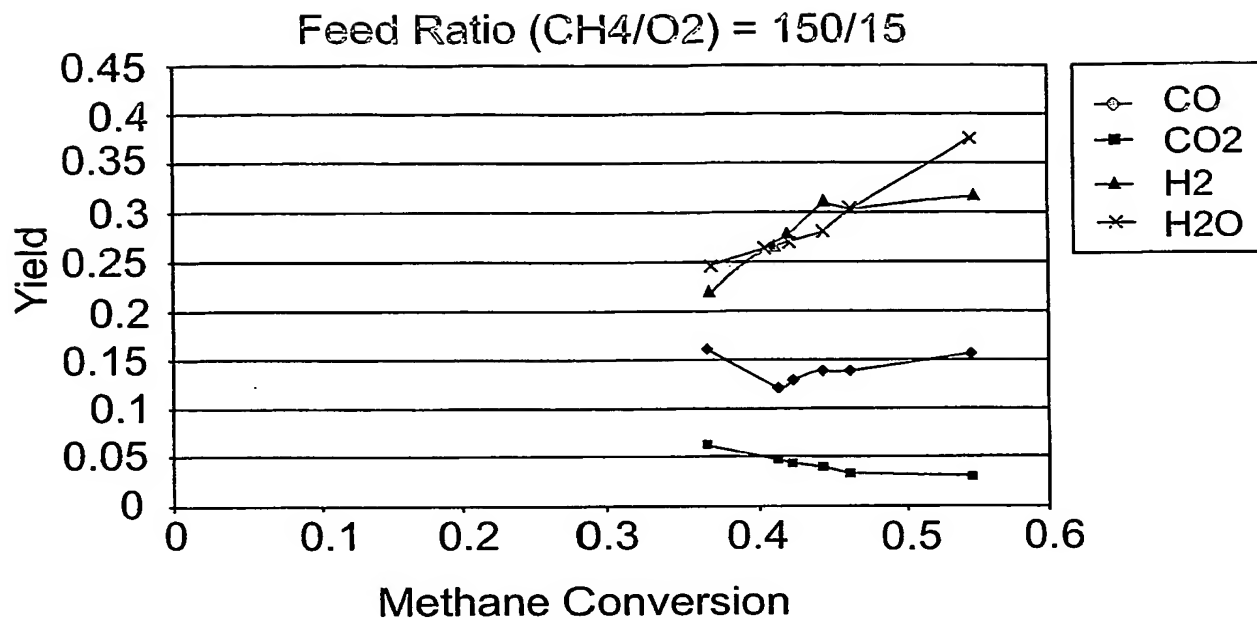


Fig. 11

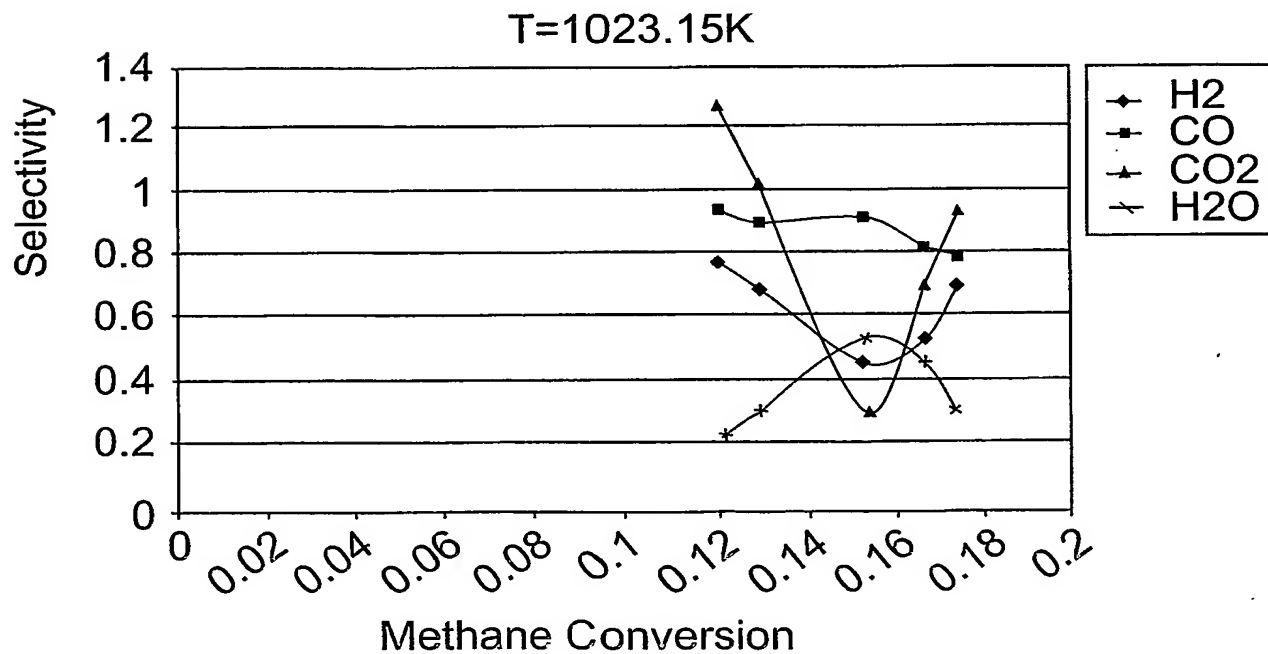


Fig. 12

13 / 15

T=1023.15K

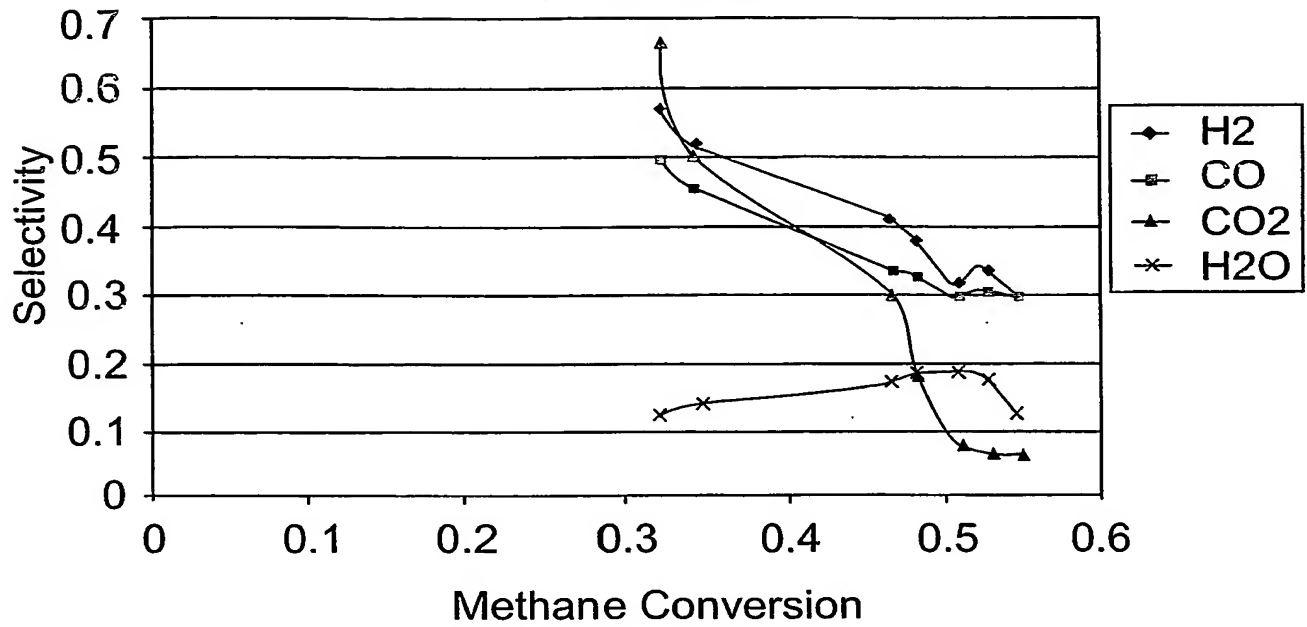


Fig. 13

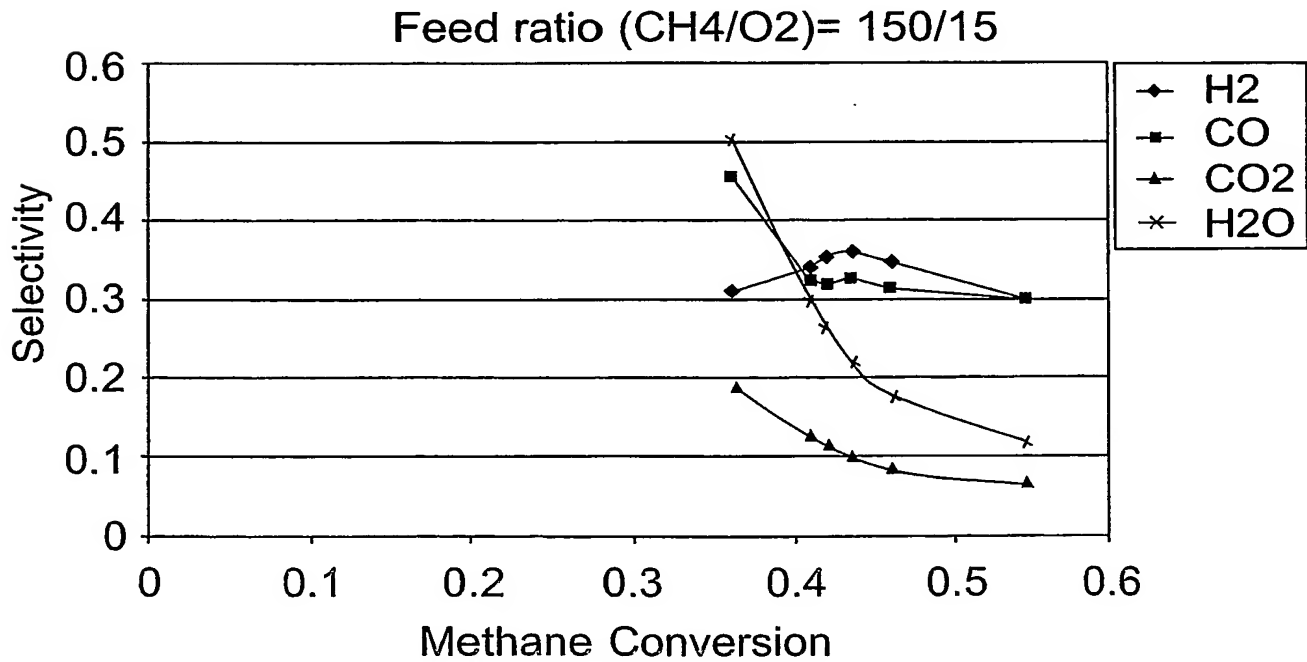


Fig. 14

14 / 15

T = 1023.15K

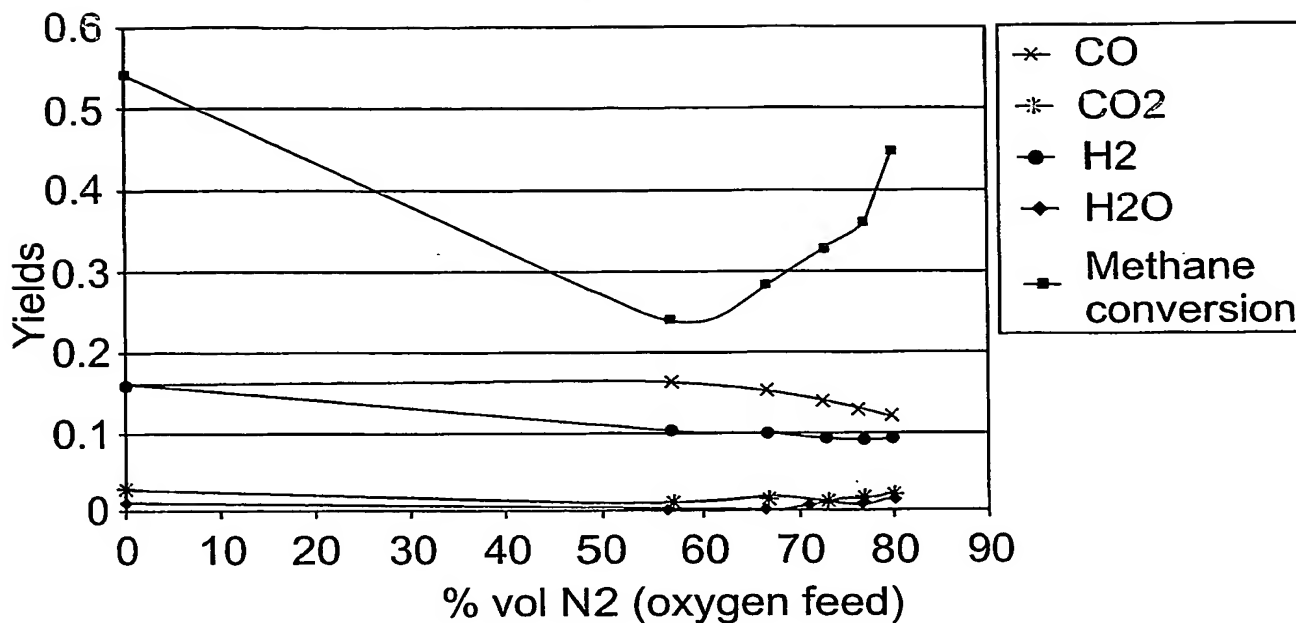


Fig. 15

T = 1023.15K

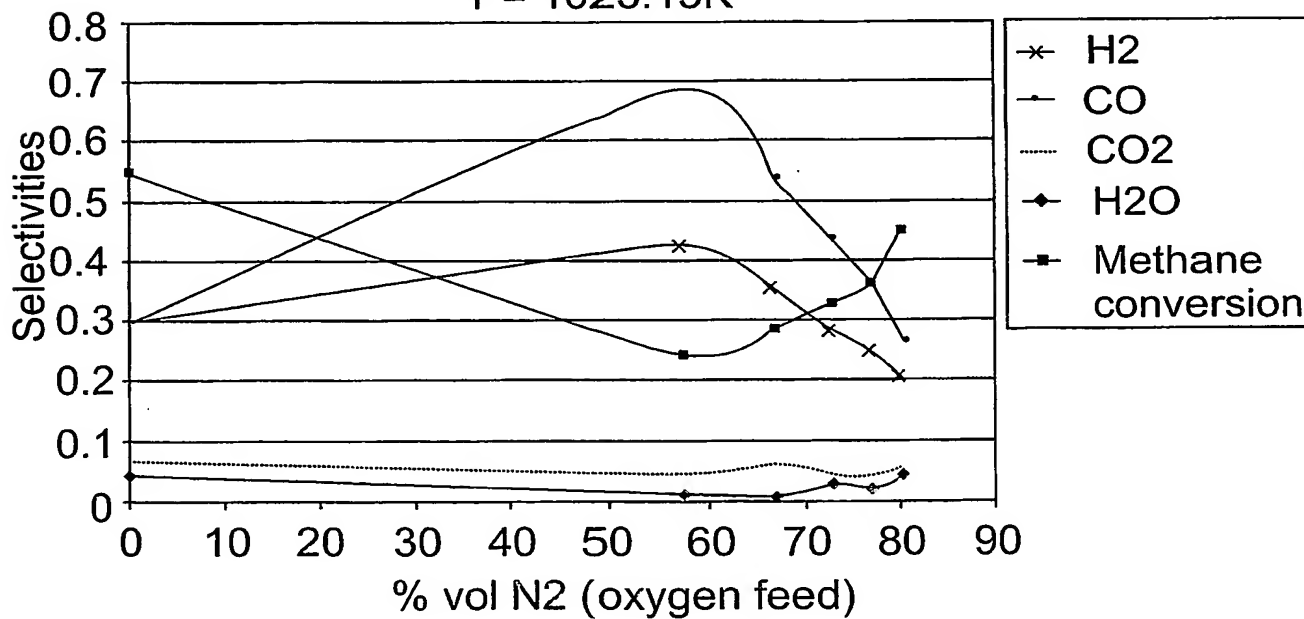


Fig. 16

15 / 15

T = 1023.15K

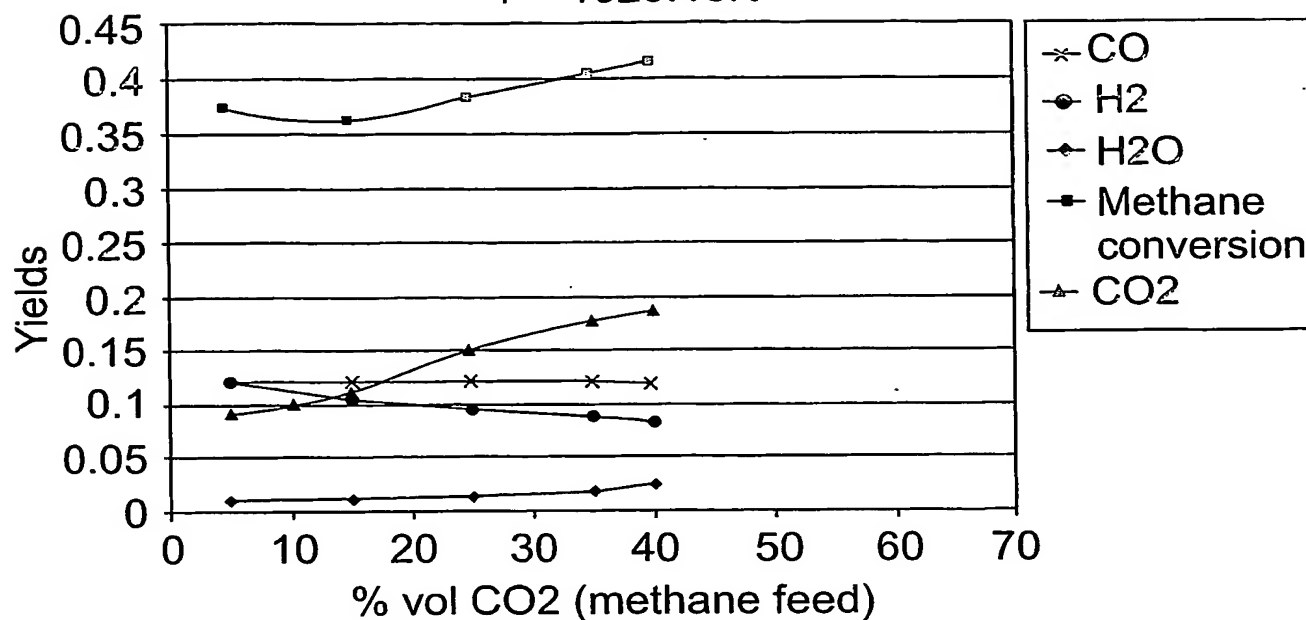


Fig. 17

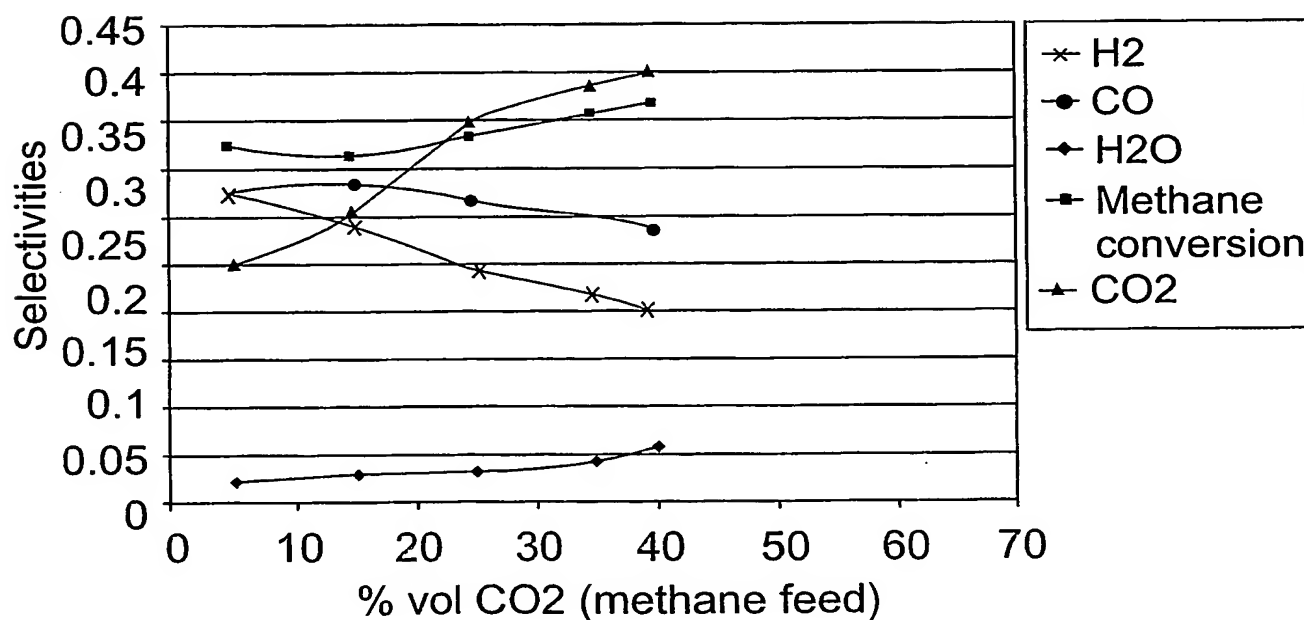


Fig. 18

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB2004/001787

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01D53/22 B01D69/02 C01B3/38 C01B13/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>WO 01/93987 A (PRAXAIR TECHNOLOGY INC) 13 December 2001 (2001-12-13) cited in the application</p> <p>page 3, line 27 - page 4, line 23 page 10, line 19 - page 11, line 24 page 12, lines 1-4 page 13, line 12 - page 17, line 9; figures 1-3</p> <p style="text-align: center;">----- -/--</p>	<p>1-4, 8, 10-14, 17, 19-25, 28, 29</p>

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

24 September 2004

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

International Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>EP 0 663 232 A (AIR PROD & CHEM) 19 July 1995 (1995-07-19)</p> <p>page 3, lines 6-25,42 page 5, lines 17-52 page 7, line 51 - page 8, line 1; example 8</p>	<p>1-4,8, 12-14, 17, 21-25, 28,29</p>
X	<p>US 5 846 641 A (ZHOU MINYAO ET AL) 8 December 1998 (1998-12-08)</p> <p>column 1, line 57 - column 2, line 19</p>	<p>1-3,14, 17, 21-25, 28,29</p>
X	<p>US 2002/022568 A1 (MACKAY RICHARD ET AL) 21 February 2002 (2002-02-21)</p> <p>paragraphs '0003!, '0004!, '0024!, '0030!, '0035! - '0037!, '0042!, '0046!; example 4</p>	<p>1-3,8, 12-14, 17, 19-26, 28,29</p>
P,X	<p>WO 03/099424 A (STATOIL ASA ; BP CORP NORTH AMERICA INC (US)) 4 December 2003 (2003-12-04)</p> <p>page 1, line 19 - page 2, line 34 page 5, line 4 - page 6, line 10 page 7, line 18 - page 8, line 13; figure 1 page 12, line 27 - page 14, line 23; example</p>	<p>1-3,8, 11-14, 17, 19-25, 28,29</p>
A	<p>US 5 980 840 A (KOBYLINSKI THADDEUS P ET AL) 9 November 1999 (1999-11-09) column 1, line 28 - column 3, line 3 column 6, line 7 - column 7, line 48</p>	<p>1-40</p>

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International Application No
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